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(54) Title: HALOGEN-FREE FLAME-RETARDANT THERMOPLASTIC POLYESTER OR POLYAMIDE COMPOSITION

(57) Abstract

The invention relates to a flame-retardant polyester or polyamide composition that contains a combination of a compound derived from triazine and an organic phosphorus compound. By choosing as the triazine compound a melamine condensation product, for example melam, a UL 94 V-0 and GWFI 960° classification can be obtained for glass-fibre reinforced polyester or polyamide with a relatively low concentration of flame-retardant additives, and without good mechanical properties being affected. Moreover it is unusual that the CTI value can again be brought to 600 Volt for this glass-fibre reinforced polyester or polyamide. In a preferred embodiment use is made of a phosphorous-containing compound containing more than 14 wt.% P. The use thereof with for example melamine cyanurate results in optimum flame-retardant behaviour at a low total concentration of flame-retardant additives. Important additional aspects are improved crystallisation behaviour and a high stiffness.

Woonhuis v. Flammewicht

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HALOGEN-FREE FLAME-RETARDANT THERMOPLASTIC

5 POLYESTER OR POLYAMIDE COMPOSITION

The invention relates to a halogen-free, flame-retardant thermoplastic polyester or polyamide 10 composition that contains a combination of organic phosphorus compound and a nitrogen-containing flame retardant.

Such a composition is known from EP-A-672,717. This describes a flame-retardant 15 polybutylene terephthalate, PBT, composition in which the organic phosphorus compound is a hydroquinone type of aromatic oligo- or polyphosphate and the nitrogen-containing flame retardant is a salt of a triazine derivative with at least one acid of cyanuric acid or 20 isocyanuric acid. In the examples melamine, benzoguanamine and acetoguanamine are used as the triazine derivative. To obtain a UL-94 V-O classification, the compositions contain approx. 20 parts by weight of organic phosphorus compound and at 25 least 8 parts by weight of triazine derivative per 100 parts by weight of PBT. With glass fibre present in the composition the required concentration of flame retardant combination was at least approx. 40 parts by weight per 100 parts by weight of PBT with 30 parts by 30 weight of glass fibre.

Such high concentrations of flame retardant combination have a highly adverse influence on the polymer composition's mechanical and processing properties. For example, a value of at least 50°C was 35 found for the difference between T_m and T_c , T_m = melting point and T_c = crystallisation temperature, measured with differential scanning calorimetry (DSC),

for the PBT-based compositions according to the aforementioned state of the art. For PBT without a flame retardant this difference is 35-40°C resulting in a shorter cycle time in injection moulding. It is also 5 known that organic phosphorus flame retardants, which are fluid at room temperature, have an adverse effect on the polymer composition's stiffness.

The invention's object is hence a halogen-free flame-retardant thermoplastic polyester or 10 polyamide composition that does not present the aforementioned drawbacks, or possesses them to a substantially lesser extent.

The invention's object is achieved with a flame retardant combination that is characterised in 15 that the compound derived from triazine is a melamine condensation product, preferably melam or melem. The invention also covers a halogen-free glassfibre reinforced thermoplastic polyamide composition in which the flame retardant combination is characterised in 20 that the organic phosphorus compound contains at least 14 wt.% phosphorus and the compound derived from triazine is melamine cyanurate.

In principle, all the current thermoplastic polyesters and copolyesters and polyamides can be used 25 as the thermoplastic polyester or polyamide for the composition. Examples of this are polyalkylene terephthalates or copolyesters thereof with isophthalic acid, for example polyethylene terephthalate, PET, polybutylene terephthalate, PBT, polyalkylene 30 naphthalates, for example polyethylene naphthalate, PEN, polypropylene naphthalate, polybutylene naphthalate, PBN, polyalkylene dibenzoates, for example polyethylene bibenzoate and copolyesters hereof.

Preferable are PET, PBT, PEN and PBN. Also suitable are block copolymers which, in addition to hard polyester segments from the above group of thermoplastic polyesters, also contain soft polyester segments

5 derived from at least one polyether or aliphatic polyester. Examples of such block copolymers with elastomeric properties are for example described in "Encyclopedia of Polymer Science and Engineering", Vol. 12, p. 75 ff. (1988), John Wiley & Sons and

10 "Thermoplastic Elastomers", 2nd Ed., chapter 8 (1996) Hauser Verlag and the references mentioned therein.

Polyamides useful in the practice of this invention include those which are well-known in the art, and for instance described in Encyclopedia of

15 Polymer Science and Technology, Vol. 11, p.315, (1988) ISBN 0-471-80943-8 (V.11). The invention is especially very effective in polyamides having a melting point of higher than 265°C. For instance polyamide 4.6 and the copolyamides based on aliphatic and aromatic

20 dicarboxylic acids. Examples thereof are polyamide 6/6.T, 6.6/6.T, 6.6/6/6.T, 6.6/6.I/6.T etc.

Melamine condensation products are for example melam, melem, melon and menthone and can for example be obtained with the process described in

25 WO-A-96/16948. Preferably the dimer, melam, or the trimer, melem, is used.

In the combination with a melamine condensation product the phosphorus compound can be chosen from the wide group of organic phosphates, phosphites, phosphonates and phosphinates. Preferably use is made of phosphates and phosphonates. Examples of such compounds are described in for example Kirk Othmer, Encyclopedia of chemical technology, Vol. 10, p.396 ff. (1980).

A large number is commercially available, for example resorcinolbis(diphenylphosphate) oligomer, under the trade name Fyrolflex RDP from AKZO-Nobel, NL; cresyldiphenylphosphate, CDP, under the trade name 5 Kronitex CDP from FMC, UK; trimethylolpropanol ester of methyl phosphoric acid, under the trade name Amgard P45 from Albright and Wilson, USA; poly(pentaerythritol phosphonate under the trade name Cyagard RF 1041 from American Cyanamid, USA. Hostaflam OP 910; a mixture of 10 cyclic di- and triphosphonates containing 21 wt.% P, from Hoechst, Germany.

It is particularly advantageous to use an organic phosphorus compound with a phosphorus content of at least 14 wt.%; preferably 18 wt.%. An example of 15 this are Amgard P45, and the metal phosphinates as for instance in US-A-4,208,321 and US-A-3,594,347.

A practical requirement for the organic phosphorus compound is a low volatility at the processing temperatures of the polyester or polyamide 20 composition and the service temperature of objects obtained from the composition. For this reason cresyldiphenylphosphate, for example, is less suitable for guaranteeing flame-retardant behaviour in the longer term.

25 The compositions of the invention can be obtained in a simple way by means of mixing in the melt. Use is then preferably made of an extruder fitted with means that make it possible to dose the phosphorus compound, which is usually fluid at room temperature 30 already. It is also advantageous if fibrous reinforcing materials can be dosed to the melt separately. It is also possible that the flame retardant components are already present in the polymerisation process for the production of the polyamide or polyester.

The concentration of organic phosphorus compound may vary within a wide range, for example between 0.5 and 20 wt.%, preferably between 1 and 12 wt.%, even more preferably between 2 and 10 wt.%. The 5 concentration of the compound derived from triazine may vary within a wide range, for example between 2 and 25 wt.%, preferably between 3 and 20 wt.%, most preferably between 4 and 16 wt.%. Weight percentages are relative to the composition's total weight. A person skilled in 10 the art will be able to determine the optimum composition in his case through systematic research.

The compositions according to the invention may furthermore contain the usual additives, for example heat stabiliser, UV stabilisers, pigments, 15 processing agents, for example mould release agents, and fillers, for example clay and reinforcing fibres, for example glass fibres. More substances that improve the flame-retardant behaviour may optionally be added, for example char-forming substances such as 20 polyphenylene ether and polycarbonate and substances that have an effect on the dripping behaviour, for example fluoropolymers such as polytetrafluoroethylene. Well-known stabilisers are for example hindered phenols.

25 In the presence of glass fibre reinforcement in particular the compositions according to the invention show surprising advantages. For example, the CTI, comparative tracking index, increases from approx. 350 Volt to 600 Volt, which presents particular 30 advantages in electrical applications. In addition, moduli of elasticity are realized that have never before been published for polyester and polyamide compositions based on organic phosphorus-containing

flame retardants with comparable flame-retardant behaviour.

The invention will now be further elucidated with reference to the following examples and
5 comparative examples.

Materials

- PBT, $\eta_{rel} = 2.0$, measured in m-cresol, from DSM, NL
- 10 PA-6 nylon-6, having a relative viscosity, $\eta_0 = 2.3$ (in formic acid)
- PA-6.6 nylon-6.6, having a relative viscosity, $\eta_0 = 2.4$ (in formic acid)
- 15 PA-4.6 Stanyl® KS 200, $\eta_0 = 2.3$ (in formic) of DSM
- PA-6.6/6.T/6.I Amodel® A 1133 HS, containing 33 wt% glassfibre, of AMOCO
- resorcinol (bis-biphenylphosphate), Fyroflex RDP®
- 20 from AKZO-Nobel. P content = 10.5 wt.%
- cresyldiphenylphosphate, Kronitex CDP, from FMC, USA. P content = 8.9 wt.%
- Zn-salt of dimethyl phosphonic acid, (DMPA) was prepared from DMPA from Aldrich and Zn-acetate. P
- 25 content = 22 wt.%.
- trimethylolpropanol ester of methylphosphoric acid, Amgard® P45, from Albright and Wilson, USA. P content = 20.8 wt.%
- melam from DSM, the Netherlands. Particle size d_{50}
- 30 = 4 μm
- melamine cyanurate from DSM, $d_{50} = 8 \mu\text{m}$
- glass fibre, length 4.5 cm, diameter 11 μm , PPG 3786 from PPG, France

Compounding

The compositions were mixed using a ZSK 30/39 D corotating twin-screw extruder with degassing 5 at a set temperature of 250°C voor PBT and PA-6, 280°C for PA-6.6 and 300°C for PA 4.6 en PA 6.6/6.T/6.I. 10 kg/hour throughput at a speed of 200 rpm. Ground PBT or polyamide and solid components were premixed in dry condition and dried for 24 hours at 90°C. Glass fibre 10 was dosed separately via a side feed. The fluid phosphorus compounds were injected with the aid of a dosing pump. Amgard P45 was to that end diluted with acetone.

15 Injection-moulding

Prior to the injection-moulding the granules obtained by compounding in the extruder were dried for 24 hours at 90°C.

An injection-moulding machine of type Engel 20 80 A was used for the injection-moulding at set temperatures of 235-245°C for PBT and PA-6, 280-300°C for PA 6.6 and 280-330°C for PA 4.6 and PA 6.6/6.T/6.I. The mould temperature was 90°C. Dimensions:
- UL-94 specimens: thickness 1.6 and 0.8 mm, resp.
25 - tensile test specimens: thickness 4 mm
- glow wire test plates: 1 mm thickness

Tests

The following properties of the injection-30 moulded specimens were determined:
Flammability: UL-94, GWFI (glow wire flammability test) according to ISO-IEC 695-2-1.

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Mechanical properties: tensile test according to ISO 527/1 using dry-as-moulded samples.

Differential scanning calorimetry, DSC, was carried out at a scanning speed of 20°C/minute from -110°C to 250°C, 5 after 10 minutes at 250°C, cooled at the same speed of 20°C/minute. The crystallisation temperature, T_c , was determined in the cooling curve, the melting point, T_m , was determined in the 2nd heating curve.

CTI, the comparative tracking index, was measured 10 according to ISO IEC 112.

Compositions and results

They are given in Table 1 for PBT, as far as flame-retardant behaviour, mechanical properties, CTI and T_m - T_c are concerned.

TABLE 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
PBT 5007 [wt. %]	100	80	82.5	80	90	81	85	45	45	49	45	45	50	54
Mecy [wt. %]		10	12.5		15	7.5	15	15	15					
Melam [wt. %]										15	15	15	8	8
Fyroflex RDP [wt. %]			7.5					10			10			
CDP [wt. %]		7.5												
Amgard P45 [wt. %]			10	4	7.5			10	6		10	12		
$[(Zn((CH_2)_2PO_2)_2)_x]$													8	
PPG 3786 [wt. %]		20						30	30	30	30	30	30	30

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
UL-94	N.C.	N.C.	V-0	V-0	V-2	V-0	N.C.	V-2	N.C.	N.C.	V-0	V-0	V-0	V-0
(1.6 mm 48 h. 23°C/50% RH)	-	-	V-0	V-0	V-2	V-0	-	V-2	N.C.	N.C.	V-0	V-0	V-0	V-0
(1.6 mm 168 h. 70°C/50% RH)			V-0	V-0	V-0	V-0	V-0	-	-	-	-	-	-	-
(0.8 mm 48 h. 23°C/50% RH)			V-0	V-2	V-0	V-0	V-0	-	-	-	-	-	-	-
(0.8 mm 168 h. 70°C/50% RH)	N.C.	N.C.	-	-	V-2	V-0	V-0	-	-	-	-	-	-	-
GWFI (1 mm)	-	-	960	960	960	960	960	750	960	960	960	960	960	960
elongation at break [%]	100	3.5	23	17	9.4	3.2	5.4	3.1	2.0	2.2	2.8	2.5	2.5	2.8
E-modulus [N/mm ²]	2700	7000	1705	2036	2100	3100	2600	8200	8600	10300	8100	9600	10100	11000
tensile strength [N/mm ²]	55	120	37	40	53	53	51	85	92	105	80	105	110	118
CTI [Volt]	600	375	-	600	-	-	-	-	-	600	-	600	-	600
T _m - T _c	35 - 40	-	-	36	-	-	-	-	15	17	-	30	-	-

In Table 1 N.C. stands for 'no classification according to UL-94' (glow wire flammability test). If a measurement was not conducted, this is indicated by a dash: -.

5 The results obtained for the non-reinforced compositions reflect the superior effect of Amgard P45 relative to the RDP, in terms of the flame-retardant properties, tensile strength and stiffness.

Composition 3 containing

10 cresyldiphenylphosphate, P content 8.9%, also showed good flame-retardant behaviour relative to composition 4, but coupled to a very low stiffness. These flame-retardant properties could however not be retained in time because the cresyldiphenylphosphate is too
15 volatile and gradually disappears with the composition. The advantages of Amgard P45 combined with melamine cyanurate are also clearly observable in glass-fibre reinforced compositions.

In the glow wire flammability test (GWFI)
20 composition 8 was ignited at 750°C already; in the case of composition 10 with a substantially lower concentration of phosphorus-containing flame retardant this temperature is 960°C. A UL-94 classification V-2 can be obtained with composition 9 already.

25 When melam was used in composition 8 instead of melamine cyanurate (see composition 11), a GWFI of 960°C was measured. A UL classification of V-0 was realised for compositions 12 and 13. The great advantage in mechanical properties of the compositions
30 based on Amgard P45 is clearly observable here too (compositions 12 and 13).

Also surprising is that the glass fibre reinforcement's adverse effect on the CTI (see

composition 2) was entirely counteracted in the composition according to the invention (10 and 12).

The compositions according to the invention also showed substantially better crystallisation 5 behaviour than the compositions according to the state of the art (EP-A-672717). The composition based on melamine cyanurate in particular offers particular advantages in that respect.

When instead of the Amgard P45 the Zn-salt of 10 dimethylphosphonic acid is used in the composition 13 the same flame retardant properties are measured. The mechanical properties are improved significantly. (composition 14)

In Table 2 similar results are shown for 15 polyamides. Especially for the high melting polyamides the advantages of the combination of melamine condensation products and the phosphorus compound with a high phosphorous content are manifest. Actually it is, as far as is known by the inventors, the first time 20 that for the high melting glass fibre reinforced polyamides a non-halogen containing flame retardant composition is obtained fulfilling UL-94, V-O, that also possesses good mechanical and electrical properties.

25 In the highmelting polyamide the combination of a condensation product of melamine and a metal salt of a phosphinic acid is preferred. If the metal salt alone is been used in the polyamide only for a few metal salts and only in concentrations of at least 30 about 30 wt.% a V-O classification can be obtained for glass fibre reinforced compositions. In the combination with melam etc. with appreciably lower concentrations and for a great number of metals salts a high

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classification can be realised, thereby giving better mechanical properties.

The compositions of the invention can be moulded into objects that can find wide application.

5 Very advantageous the compositions of the invention are used in the manufacture of electric and electronic parts.

Table 2

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
PA-6	95	45	45											
PA-6.6				96	96	60	60	45						
PA-4.6										90	50	50	45	
PA 6.6/6.T/6.I														
Mecy	15	4			20									53
Melam	5	15		4		20								
Amgard P45	10	10					20	10						12
[Zn((CH ₂) ₂ PO ₂) ₂] _x														10
PPG 3786	30	30			20	20	20							8
UL-94 1,6 mm 48h 23°C/50% RH	V-O	NC	V-2	V-O	V-2	V-2	V-O	V-O	V-O	V-2	V-O	V-O	V-O	27**)
GWF1	960	850	960	960										
Elongation %	3.2	3.0												
E-modulus [N/mm ²] · 10 ³	10	10.8												11,3

	15	16	17	18	19	20	21	22	23	24	25	26	27	28
tensile strength [N/mm ²]	152	172			*				176					
CTI [V]	-	-	-	-	-	500		600		450	550			550

*) not stable in compounding. T.S. inferior

**) origine glass fibre unknown.

CLAIMS

1. Halogen-free flame-retardant glass fibre reinforced thermoplastic polyamide composition comprising a compound derived from triazine and an organic phosphorus compound, characterised in that the compound derived from triazine is melamine cyanurate and the organic phosphorus compound contains at least 14 wt.% phosphorus.
2. Flame-retardant polyamide composition according to Claim 1, characterised in that the organic phosphorus compound is a trimethylolpropanol ester of methylphosphoric acid.
3. Flame-retardant polyamide composition according to Claim 1 or Claim 2, characterised in that the concentration of melamine cyanurate lies between 2 and 25 wt.% and the concentration of organic phosphorus compound lies between 0.5 and 20 wt.%, preferably between 3 and 20 wt.% and 1 and 12 wt.%, respectively.
4. Flame-retardant polyamide composition according to Claim 3, characterised in that the concentration of melamine cyanurate lies between 4 and 16 wt.% and the concentration of organic phosphorus compound lies between 2 and 10 wt.%.
5. Halogen-free flame-retardant thermoplastic polyester or polyamide composition comprising a compound derived from triazine and an organic phosphorus compound, characterised in that the compound derived from triazine is a melamine condensation product.
6. Flame-retardant polyester or polyamide composition according to Claim 5, characterised in that the melamine condensation product is melam.

7. Flame-retardant polyester or polyamide composition according to Claim 5, characterised in that the organic phosphorus compound contains more than 14 wt.% phosphorus.
- 5 8. Flame-retardant polyester or polyamide composition according to any one of Claims 5-7, characterised in that the concentration of melamine condensate lies between 2 and 25 wt.% and the concentration of organic phosphorus compound lies between 0.5 and 20 wt.%, preferably between 3 and 20 wt.% and 1 and 12 wt.% of the composition, respectively.
- 10 9. Flame-retardant polyester or polyamide composition according to Claim 8, characterised in that the concentration of melamine condensate lies between 4 and 16 wt.% and the concentration of organic phosphorus compound lies between 2 and 10 wt.% of the composition.
- 15 10. Flame-retardant polyester or polyamide composition according to any one of the above claims, characterised in that glass fibre reinforcement is also present.
- 20 11. Object moulded from a composition according to one of the claims 1-10.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/NL 98/00226

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L67/00 C08L77/00 C08K5/00 // (C08K5/00, 5:3492, 5:54)

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 391 (C-1087), 22 July 1993 & JP 05 070671 A (MITSUBISHI PETROCHEM CO LTD), 23 March 1993 see abstract ---	1-4, 10
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 485 (C-1248), 9 September 1994 & JP 06 157880 A (MITSUBISHI PETROCHEM CO LTD; OTHERS: 01), 7 June 1994 see abstract ---	1-4, 10
		-/-

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Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 151305 A (MITSUBISHI CHEM CORP;MITSUBISHI ENG PLAST KK), 10 June 1997 see abstract ---	1-4,10
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P,X	DE 196 14 424 A (HOECHST AG) 16 October 1997 see claims 1-3,5,6 ---	1-4,10
	-/-	

INTERNATIONAL SEARCH REPORT

Interr ial Application No
PCT/NL 98/00226

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 42264 A (T & N TECHNOLOGY LTD ; MARTIN LEE HAMILTON (US)) 13 November 1997 see claims 1-4 -----	1-4, 10
A	DD 135 207 A (KEIL MARTIN; PAPE DIETER; VOGT HANS; JECHT WERNER; HELD ROLF WYLAND; MA) 18 April 1979 see claim 2; example 5 -----	5

INTERNATIONAL SEARCH REPORT

In international application No.
PCT/NL 98/00226

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/NL 98/00226

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-4 10 11

polyester composition characterised by
a) melamincyanurate with a number of N-atoms of 9;
number of O-atoms 3;
b) phosphoric compound with a P-content > 14 wt%

2. Claims: 5-9

polyester or polyamide composition characterised by
a) melamine-condensate with a number of N-atoms 10,
number of O-atoms 0;
b) phosphoric compound of undefined P-content;
compound a) showing therefore totally different chemical
behaviour, characteristics and properties than the compound
a) disclosed in invention part 1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 98/00226

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE 19614424 A	16-10-1997	AU 2293997 A		07-11-1997
		WO 9739053 A		23-10-1997
WO 9742264 A	13-11-1997	GB 2312900 A		12-11-1997
DD 135207 A	18-04-1979	NONE		

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